Cleaning of Aluminum After Machining with Coolants*

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ABSTRACT

An x-ray photoemission spectroscopic study was undertaken to compare the cleaning of the Advanced Photon Source (APS) aluminum extrusion storage ring vacuum chambers after machining with and without water soluble coolants. While there was significant contamination left by the coolants, the cleaning process was capable of removing the residue. The variation of the surface and near surface composition of samples machined either dry or with coolants was negligible after cleaning. The use of such coolants in the machining process is therefore recommended.

INTRODUCTION

The Advanced Photon Source storage ring vacuum chambers are made from extruded 6063-T5 aluminum alloy. During the extrusion process, a porous oxide layer is formed on the surface consisting of both MgO and Al_2O_3[1]. Currently, cleaning procedures are used which are known to effectively remove the original oxide layer. Since the chambers are presently machined dry, it is not known whether the cleaning procedures are capable of removing coolant residue. Such knowledge is desirable since there are advantages to be gained if coolants can be utilized. For instance, machining time and cleanliness requirements will be reduced. Therefore, a study was undertaken to compare the surface and near surface composition of extrusions which had been machined with coolants to samples which had been machined dry.

Two coolants were selected. A 5% solution of Trimsol® was chosen based on use by the Advanced Light Source (ALS). Electron stimulated desorption experiments conducted by ALS detected little difference in the desorption rate between samples which had no cutting oil used during machining and samples which had oil used followed by degreasing[2]. The second coolant, a 20% solution of Cimcool® , was chosen because the Argonne shops routinely use this product for aluminum work. Both coolants are water soluble and contain no undesirable chemicals.

EXPERIMENTAL

X-ray photoemission spectroscopy (XPS) was performed using a surface analysis apparatus which was equipped with a load-lock system for rapid sample introduction. The spectrometer was a hemispherical analyzer operated at 50 eV pass energy. The x-ray gun used a single magnesium anode.

The load-lock system consisted of three stages. The first stage had a quick entry door and could be pumped down to 10^{-2} Torr in less than five minutes after the samples were introduced. The second stage was accessed by a gate valve and routinely obtained pressures of 1×10^{-8} Torr. The final stage, the analysis chamber, was separated from the preparation stage by a gate valve. The typical operating pressure for the analysis chamber was 1×10^{-10} Torr.

The samples were cut from extrusions of 6063-T5 alloy and machined by milling to a 1 cm square, 1 mm thick. The machining, either with or without coolant, was performed on the outside of the extrusion. The inside surface, i.e., the vacuum side of the extrusion was untouched but was easily splashed with coolant solution as the outside surface was machined.

Twelve experimental conditions were evaluated. Samples were divided into two main categories which consisted of samples which did or did not undergo cleaning. Within this arrangement, samples were separated into three groups. The first group incorporated samples which were dry machined. The second group contained Trimsol machined samples, while the third group contained samples machined with Cimcool. Photoemission data was taken on the inside and outside surface for each machining procedure. Five samples were evaluated in each grouping.

Following the manufacturers' recommendations, a 5% solution of Trimsol and a 20% solution of Cimcool were employed. The coolants were misted onto the samples in order to reduce the rate of tool corrosion which can result from exposure to dilute solutions. It should be noted that the manufacturer's literature on Cimcool states

that it provides superior tool life compared to straight cutting and soluble oils. No such claims are made by the Trimsol literature.

The samples were cleaned using the system developed at LEP[1]. First, the sample was degreased and then sonicated in a 2% solution of Almeco® for 4 minutes. After rinsing with deionized water, the samples were immersed in a 2% solution of Amklene® for 6 minutes. A second rinsing in deionized water followed before the samples were air dried. After drying, all the samples were placed into a clean glass vial and the vial was evacuated to approximately 1×10^{-2} Torr using a "dry" pump.

The amount of time any one sample was exposed to the atmosphere was approximately two hours. The two hours accumulated during air drying, transportation to the surface spectroscopic chamber, and subsequent loading of the samples into the chamber. It is to be expected, therefore, that the amount of carbon and oxygen present on or near the surface will be greater than literature values for samples loaded into a system immediately after cleaning. A calibration scheme was devised (to be discussed later) by which the carbon and oxygen intensity could be solely attributed to atmospheric exposure rather than coolant residue.

RESULTS AND DISCUSSION

Table I compares the machining conditions for dry and coolant machining. A surface finish of 63 microinches was specified, and the feed rate was adjusted by the shop for the three conditions in order to obtain the surface finish desired. The use of coolants increased the feed rate by approximately 15%. The reader should be cautioned that machining time is not a linear function of feed rate. While the 15% reduction in feed rate indicates that the use of coolants speeds up the machining process, the exact percentage of machining time which will be saved depends on additional variables.

In order to compare the amount of carbon and oxygen on or near the aluminum surface, the signal intensities of the peaks were multiplied by sensitivity factors which take into account the difference in excitation cross-sections for the different atomic species and transmission factors of the spectrometer. For the purposes of this report, the sensitivity factors used are those listed in the Phi handbook[3]. Strictly speaking, those factors are not entirely correct because the transmission profile for the hemispherical analyzer differs from the cylindrical mirror analyzer (CMA) used to calculate the sensitivity factors. However, this study was designed to compare dry machined versus coolant machined samples thereby negating any of the slight inaccuracies resulting from the use of CMA parameters.

The amount of carbon, oxygen, and aluminum detected was calculated from the signal intensity of the C(1s), O(1s) and Al(2p) peak areas, respectively. As a result, the reported percentage of aluminum will be lower than literature values, whereas the reported percentages for carbon and oxygen will be higher[4,5]. This discrepancy results from the fact that the Al(2s) signal intensity was not included in the calculation.

Since the samples were exposed to air during drying and were transported to the surface spectroscopic apparatus, a determination of the amount of contaminant due to air exposure was necessary. Calibration of the amount of carbon and oxygen was accomplished by argon ion sputtering a blank sample, i.e., a sample cut from the inside of the extrusion, until the surface was mostly clean, as shown in Figure 1. The peak at approximately 245 eV binding energy results from argon which has been implanted into the sample during the sputtering process. The less intense signal associated with the Al(2p) and Al(2s) peaks are loss peaks.

The binding energy of all peaks has shifted to higher energies. This shift is due to charging which resulted from the sample mounting method. Graphite, which provides electrical continuity, is commonly used to mount samples. However, because of concerns that graphite might contribute to the carbon signal, it was not employed in this study. Instead, double-sided tape was used which did not provide good contact between the sample and the mount. Charging occurred as a result. The amount of charging was determined from the binding energy shift of the C(1s) peak. Adventitious carbon exhibits a C(1s) peak at 284.6 eV binding energy if no charging is present. In this study, the C(1s) peak was measured as having a binding energy of 290.5 eV. All peaks were shifted to higher binding energy by approximately 6 eV. This magnitude of binding energy shift due to charging effects is not unreasonable. Additionally, charging typically does not effect peak shape.

Ghost peaks are present in the spectra. These peaks originate from x-rays produced from the copper mount of the x-ray anode. Small peaks result which correspond to the most intense spectral peaks but which are displaced by a characteristic energy interval. For a copper source, the most intense peaks have ghosts at 323 eV higher binding energy. For example, the peak at approximately 617 eV binding energy is a ghost result from the C(1s) peak at 290.4 eV binding energy.

After the sample was sputtered to remove the carbon, oxygen, and other contaminates below the detection limit, it was removed from the system through the load-lock and exposed to air for 15 minutes. The resultant amount of oxidation and carbon coverage is depicted in Figure 2. Figure 3 indicates the amount of carbon and oxygen present after two hours, i.e., the average time of atmospheric exposure the samples experienced. The percentage of carbon, oxygen and aluminum on or near the surface, calculated as previously described, was 13%, 42%,

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and 45%, respectively, after two hours. The signal intensity for carbon and oxygen of the twelve study groups will be calibrated against these signal intensities determined from Figure 3.

Figures 4 through 9 show representative spectra for samples which were not cleaned after dry machining and machining with either Trimsol or Cimcool. Figures 4, 5 and 6 are spectra for the outside, i.e., the machined surface, while Figures 7, 8, and 9 are spectra from the inside surface, i.e., the vacuum side of the extrusion. As evident from all the spectra, the carbon and oxygen peak intensities are greater than the calibrated spectrum of Figure 3. In addition, other species were detected on or near the surface. Most notably, Zn, Si, P, and Mg appeared. In the case of samples machined with Cimcool (Fig. 9), bismuth was also detected on two of the five samples. For the sake of clarity, the small contaminant peaks are identified in the figure captions rather than labelled on the figures. Not surprisingly, the inside surfaces (Fig. 7 - 9) showed higher concentrations of Mg. This fact was anticipated since the porous aluminum oxide layer, which results during the extrusion process, had not been etched away. Magnesium has been reported to be a large component of that porous layer[1]. The outside surface had very little detectable Mg present since the porous layer was removed during machining.

Table II compares the relative peak intensities between carbon, oxygen, and aluminum for the samples which were not cleaned. In the case of samples contaminated with other atoms or molecules such as in Figure 6, the table simply lists intensive contamination since the value of the carbon, oxygen and aluminum can be non-linearly affected by the presence of other adsorbates. Note, however, that five samples were studied for each group even though all the percentages are not listed.

Figures 10 through 15 are spectra from the samples which have been cleaned. Figures 10, 11, and 12 are from the machined surface while Figures 13, 14, and 15 are from the inside, vacuum surface. The contaminant peaks have been removed by the cleaning procedure and the percentages of O, C, and Al are close to the calibration values of Fig. 3 (see Table III). While the carbon percentage is marginally higher for the cleaned samples than the sputtered sample, the dry machined and coolant machined samples show very little variation in their surface composition. Therefore, the cleaning process is strong enough to remove the residue left behind on the surface of the extrusion by the dilute coolant solution.

If Figures 10 - 15 are analyzed in detail, it can be seen that small peaks at 941 and 962 eV binding energy appear after cleaning. These peaks are assigned to Cu(2p3/2) and Cu(2p1/2). The copper most probably originates from the bulk and diffuses to the surface during or after cleaning. Surface segregation of minority species is commonly detected and has been reported elsewhere with regards to magnesium[5].

An interesting question can be raised with regard to the segregation process. There are other methods which can initiate diffusion from the bulk. One method is by heating and repeated heating cycles, and the other is through photoinduced diffusion. Both driving forces will exist in the storage ring for the crotch absorbers and extrusion chambers. There is no information to date on the extent of the surface segregation and how much magnesium or copper, for instance, is on or near the surface after baking and photon absorption for the APS extrusions. However, it is quite possible that the secondary electron yields can be modified if enough material segregates to the surface. Figure 16 is a spectrum of the C(1s) region from Figure 13 which is a dry machined, inside surface, cleaned sample. While no curve fitting has been done, the spectrum clearly indicates at least two C(1s) peaks with binding energies of 290.5 eV and 295 eV. The peak at 290.5 eV has an asymmetric lineshape suggesting two sources of signal intensity, but without curve fitting, the assignment of two peaks within the lineshape is difficult.

Recall that due to charging effects, the adventitious C(1s) peak is detected at 290.5 eV binding energy. The origin of this peak is from dissociative chemisorption of atmospheric molecules. The C(1s) peak at 295 eV results from carbon which has been oxidized to some extent. There is only a small amount of the total carbon content which is oxidized on the surface. It is important to realize that the peak at 295 eV cannot be assigned to molecular CO based solely on the XPS data. The signal could be arising from a surface carbonate. It would be interesting, however, to determine what portion of CO desorption results from the C(1s) peak at 295 eV binding energy.

Since the activation energy for formation of CO (plus CO_2 and CH_4 for that matter) from the reaction of atomic adsorbates is high at room temperature, reactions can only occur at high temperatures or after energetic bombardment. The CO and CO_2 desorption is, therefore, most likely to be due to photoassociation reactions, or decomposition reactions if a carbonate exists, on the surface since the oxidized C(1s) peak is a small percentage of the total C(1s) signal. The same process must occur for methane desorption because methane will not chemisorb at room temperature. It is the intent of the APS surface spectroscopic effort to understand the mechanisms of desorption. Since the desorption products most probably result from surface reactions driven by energetic particle bombardment and the associated temperature increase, the goal of the research program is to reduce or eliminate desorption by modifying the surface reaction pathways.

CONCLUSION

There was little variation in the surface spectroscopic results after cleaning between samples which were dry machined versus those which were machined with coolants. Therefore, the use of coolants in the machining of the extrusions for APS is recommended.

X-ray photoemission surface spectroscopy determined that the amount of oxidized carbon on the surface is small compared to graphitic carbon. Additionally, minority species are segregating to the surface during or after cleaning. Experiments are planned which measure the secondary electron yield as a function of segregation of minority species. Furthermore, the work functions of the aluminum samples will be measured to determine if the desorption of CO, CO_2, and CH_4 can account for the decrease in the photoelectron yield after beam cleaning[6]. If not, the source of the effect will be determined and exploited.

TABLE I*

MACHINING PARAMETERS

	TRIMSOL	CIMCOOL	DRY
Recommended Speed (RPM)	4200	4200	4200
Actual Speed (RPM)	4200	4200	4200
Recommended Feed (inch/min)	25	25	25
Actual Feed (inches/min)	21.5	21	18.5
Tool Type	End Mill	End Mill	End Mill
Tool Diameter	0.625	0.625	0.625
Carbide	yes	yes	yes
Air Mist	yes	yes	---

*Conditions for machining with Trimsol, Cimcool and no coolant. A surface finish of 60 microinches was specified, and the feed rate was adjusted to achieve that finish. Use of coolant increased the feed rate by approximately 15%.

TABLE II*

Carbon, Oxygen, and Aluminum Percentages

Samples Not Cleaned

OUTSIDE				INSIDE		
			DRY MACHINED			
C	O	Al		C	O	Al
25.3	31.8	42.9		31.3	38.5	30.2
26.3	27.0	46.7		25.8	38.4	35.8
26.7	32.5	40.8		20.5	38.8	40.7
23.3	28.1	48.6		20.7	38.9	40.4
25.6	30.6	43.8		22.3	39.0	38.7
25.4	30.0	44.6	average	24.1	38.7	37.2
			TRIMSOL			
C	O	Al		C	O	Al
33.5	40.1	26.4		35.6	40.2	24.2
contaminant peaks				contaminant peaks		
			CIMCOOL			
C	O	Al		C	O	Al
35.2	30.3	34.5		53.4	29.0	17.6
43.7	27.0	29.3				
67.5	20.6	11.9		contaminant peaks		
58.5	22.8	18.7				
62.1	25.6	12.3				
53.4	25.3	21.3	average			

*The percentages of carbon, oxygen and aluminum detected for samples which had not been cleaned. In the case of extensive contamination, no values for carbon, oxygen and aluminum are given. There were five samples studied for each group. The percentages were calculated from signal intensity of the C(1s), O(1s) and Al(2p) peak areas. The Al(2s) signal intensity was not included in the calculation. As a result, the percentages for oxygen and carbon will be higher than literature values whereas the percentages for aluminum will be lower.

TABLE III*

Carbon, Oxygen, and Aluminum Percentages

SAMPLES CLEANED

OUTSIDE						INSIDE

DRY MACHINED

C	O	Al		C	O	Al
12.1	36.6	51.3		14.9	44.5	40.6
12.6	35.0	52.4		13.1	45.3	41.6
14.8	35.6	49.6		14.5	34.8	50.7
14.5	36.6	48.9		13.0	41.5	45.5
14.6	35.2	50.2		14.8	42.9	42.3
13.7	35.8	50.5	average	14.0	41.8	44.2

TRIMSOL

C	O	Al		C	O	Al
14.2	44.2	41.6		12.7	44.8	42.5
17.0	35.4	47.6		13.2	35.7	52.1
13.4	35.6	51.0		13.8	36.3	49.9
14.8	35.5	49.7		14.9	38.7	46.4
13.7	35.1	51.2		13.2	38.7	48.1
14.6	37.2	48.2	average	13.5	38.7	47.8

CIMCOOL

C	O	Al		C	O	Al
13.6	31.4	55.0		14.1	44.3	41.6
14.4	34.0	51.6		15.2	34.1	50.7
12.6	36.5	50.9		13.7	37.4	48.9
13.5	35.0	51.5		14.0	38.6	47.4
14.4	35.5	50.1		13.6	41.2	45.2
13.7	34.5	51.8	average	14.1	39.2	46.7

*The percentages of carbon, oxygen, and aluminum detected for samples which were cleaned. Percentages were calculated as described in Table II. If Al(2s) had been included in the calculation, the percentages would have been approximately 8.8%, 31.2%, and 60.0%, respectively.

REFERENCES

1.   A. G. Mathewson, LEP Vacuum Technical Note, Jan. 15, 1986.

2.   K. Kennedy, ALS Engineering Note, July 2, 1986.

3.   *Handbook of Auger Electron Spectroscopy*, Physical Electronics Inc., Eden Prairie, MN 1978.

4.   A. G. Mathewson, LEP Vacuum Technical Note, Jan. 29, 1990.

5.   N. Kaufherr, A. Krauss, D. M. Gruen, and R. Nielson, *J. Vac. Sci. Technol.*, A8, 2849, 1990.

6.   A. G. Mathewson, LEP Vacuum Technical, Note Feb., 1985.
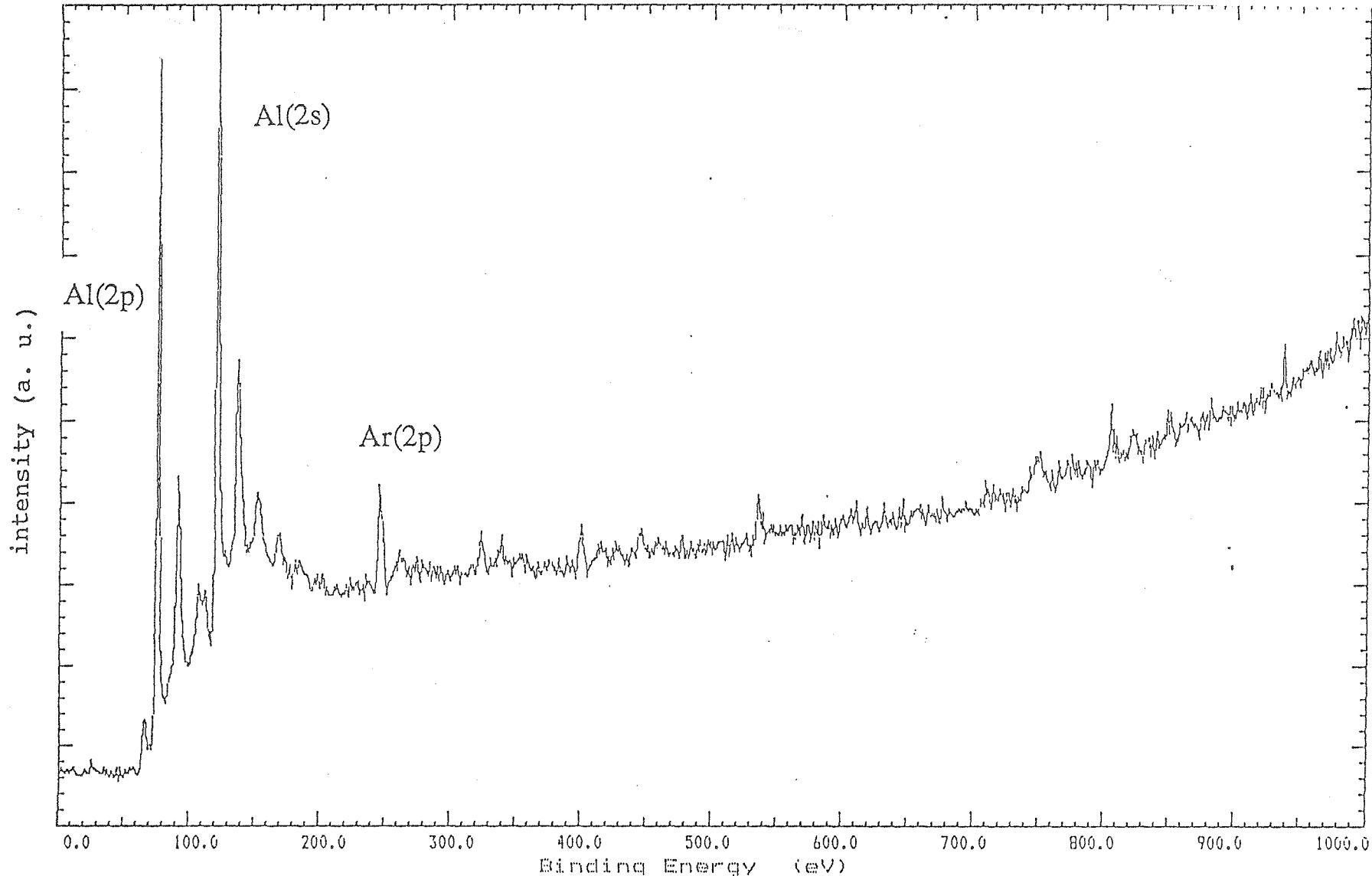
Fig. 1   XPS spectrum of a sputtered aluminum extrusion calibration sample. The sample was sputtered until the carbon and oxygen adsorbates were removed. The peak at 245 eV binding energy is due to implanted argon. The sample was mounted with double-sided tape which allowed charging to occur. As a result, the binding energies have shifted approximately 6 eV. There are ghost peaks present 323 eV above the aluminum and argon peaks due to photons from the copper mount in the X-ray gun.
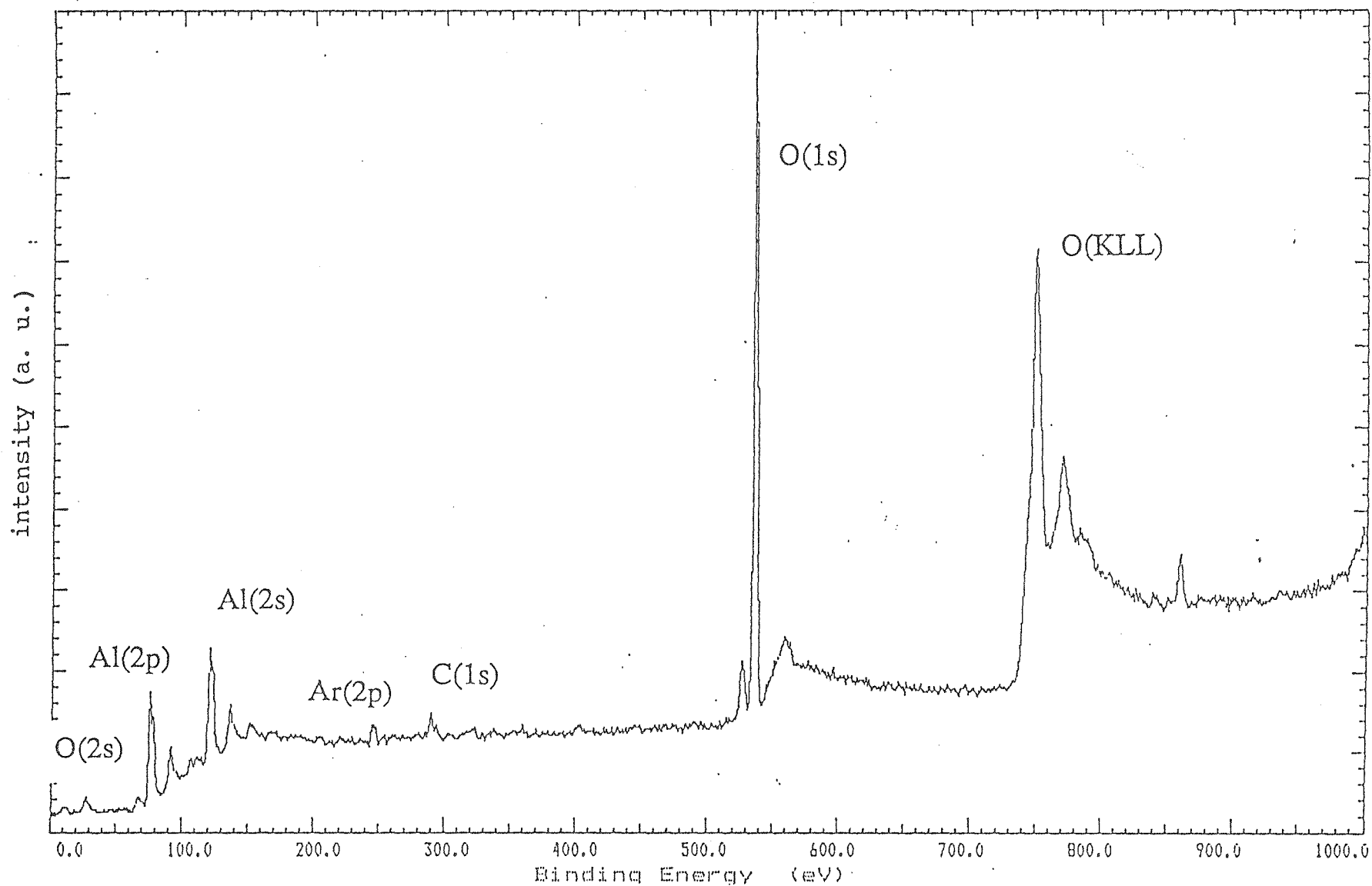
Fig. 2   Sputtered calibration sample which was removed from the vacuum chamber and exposed to the atmosphere for 15 minutes before being placed under vacuum again. Extensive oxidation has occurred along with some carbon adsorption. The ghost peak at approximately 860 eV results from the O(1s) peak. The Ar(2p) peak is still detectable.
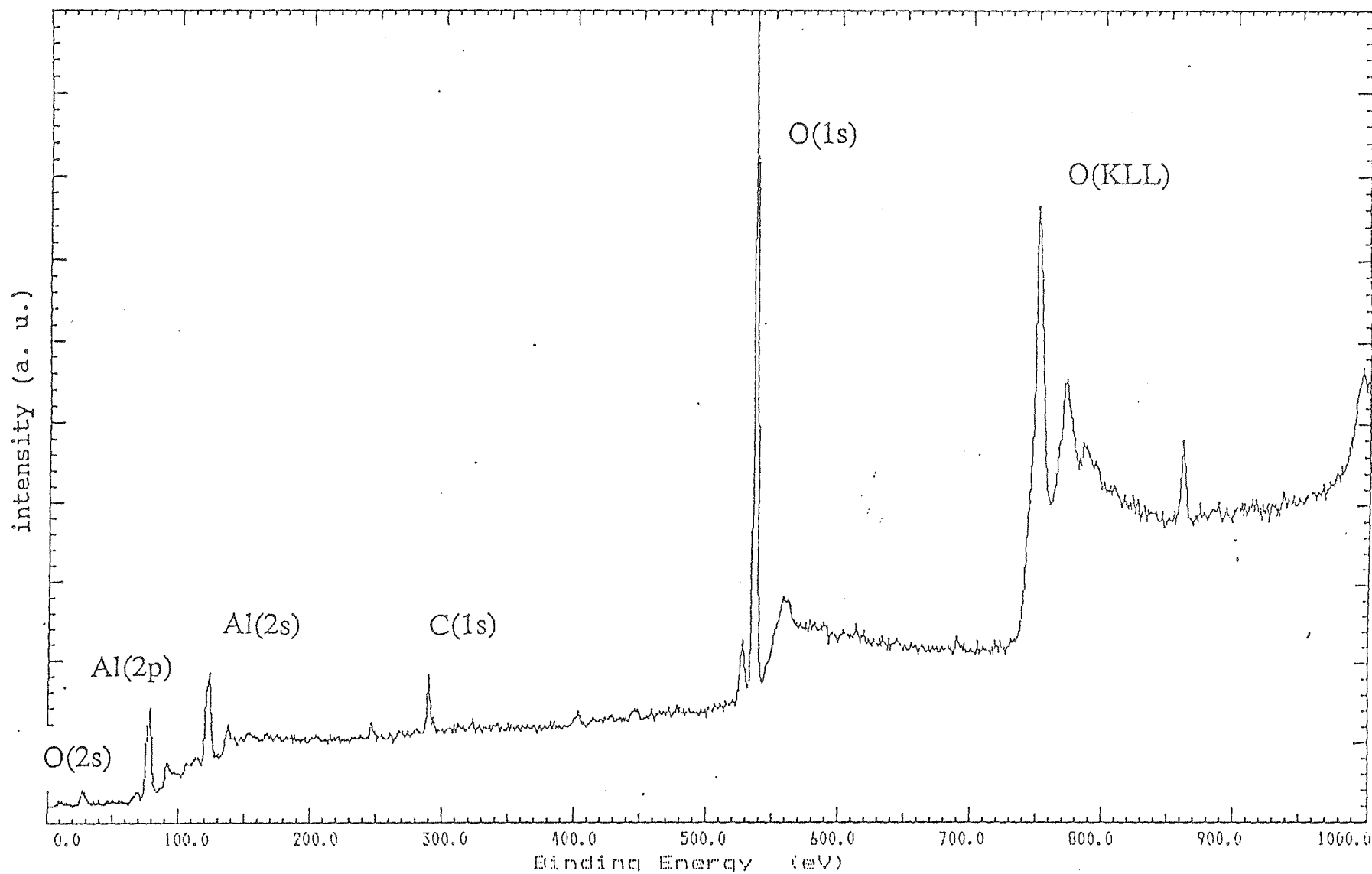
Fig. 3   Sputtered calibration sample which was removed from the vacuum system and exposed to the atmosphere for two hours. The percentage of carbon, oxygen, and aluminum is 13%, 42%, and 45%, respectively. The Al(2s) peak was not included in the calculation. If it had been, the percentages would have been 8.8%, 31.2%, and 60.0%, respectively.
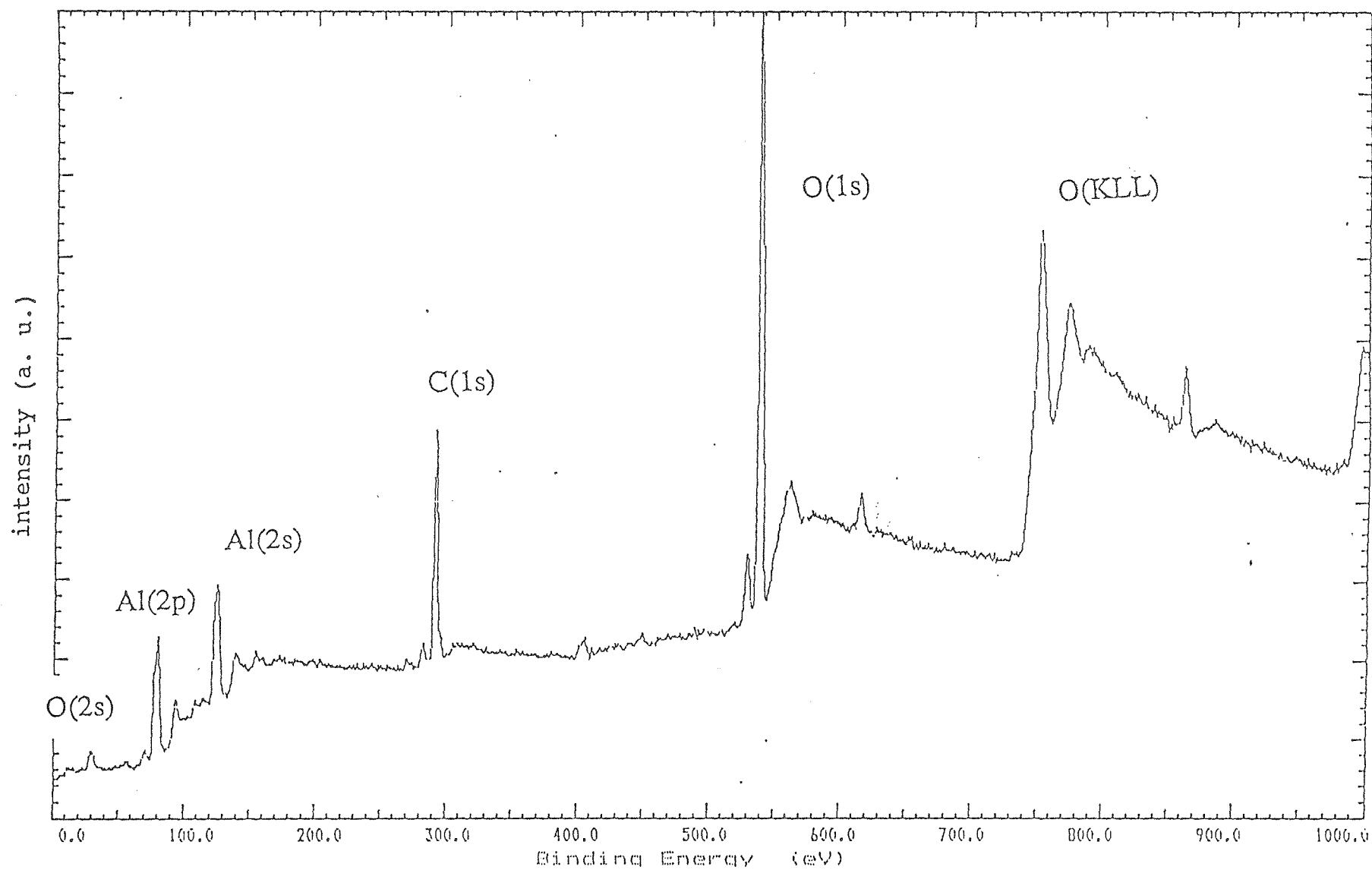
Fig. 4   The outside surface of a sample which was dry machined. Sample has not been cleaned. Since the porous aluminum oxide layer was machined away, the major contamination is carbon and oxygen.
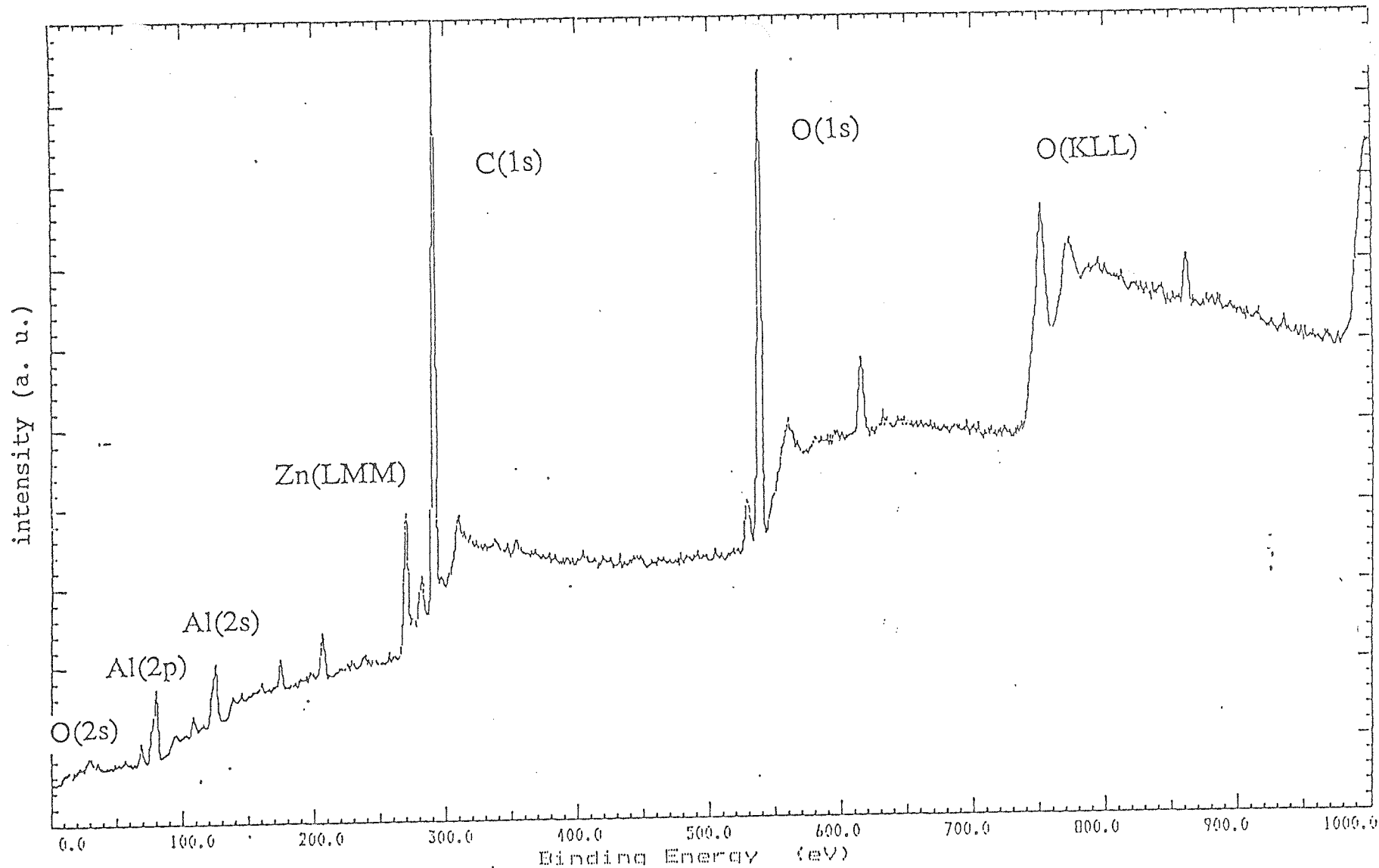
Fig. 5   The outside surface which was machined with Trimsol. Sample has not been cleaned. As a result, there are other adsorbates such as Si and P detected on or near the surface resulting from use of coolant.
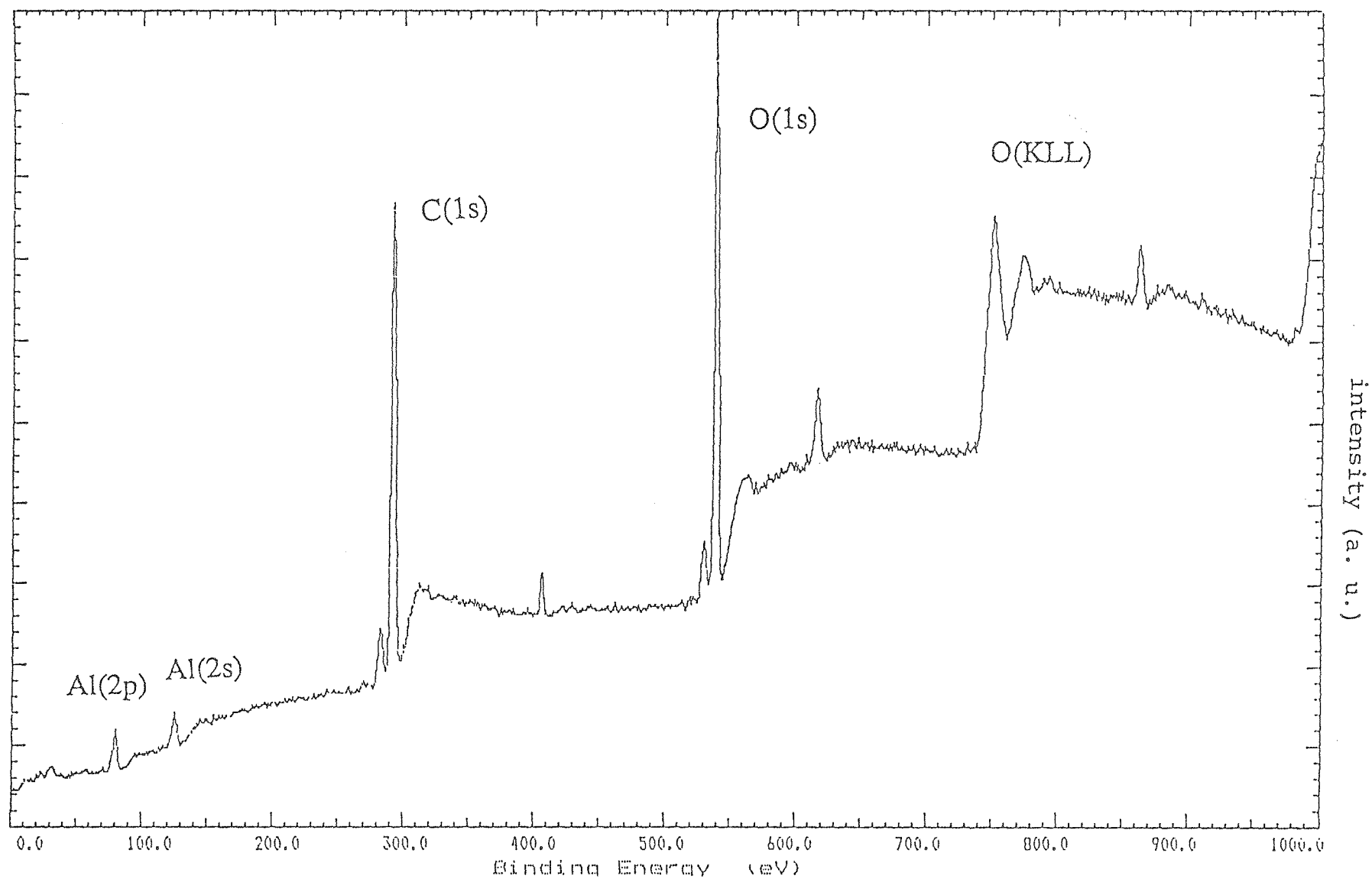
Fig. 6   The outside surface of a sample machined with Cimcool. Sample has not been cleaned. The peak at approximately 410 eV is assigned to N(1s).
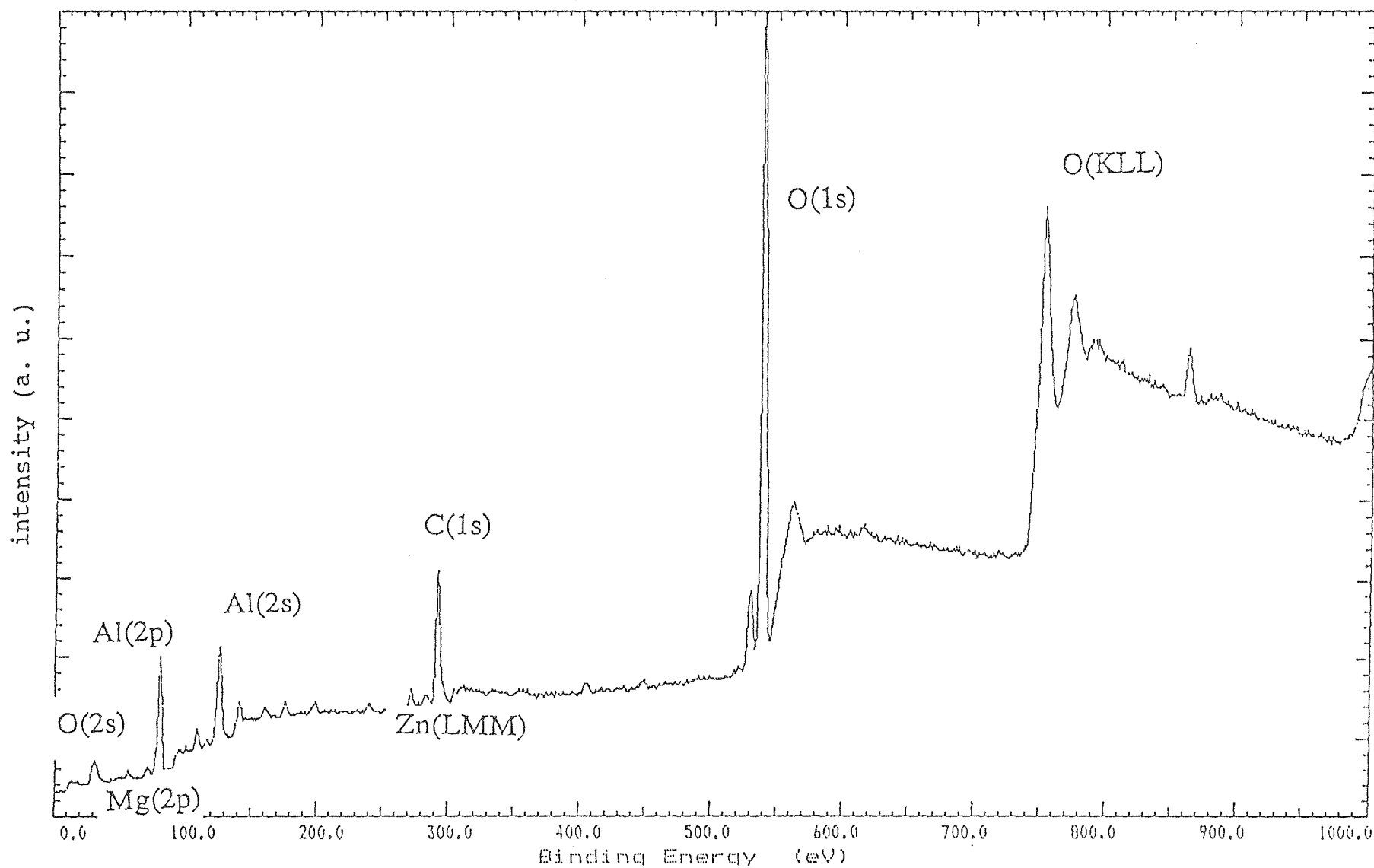
Fig. 7   The inside surface of a sample machined dry. Sample was not cleaned. Since the porous layer resulting from the extrusion layer has not been etched away, Mg, P, and Si are detectable. Zn is also present.
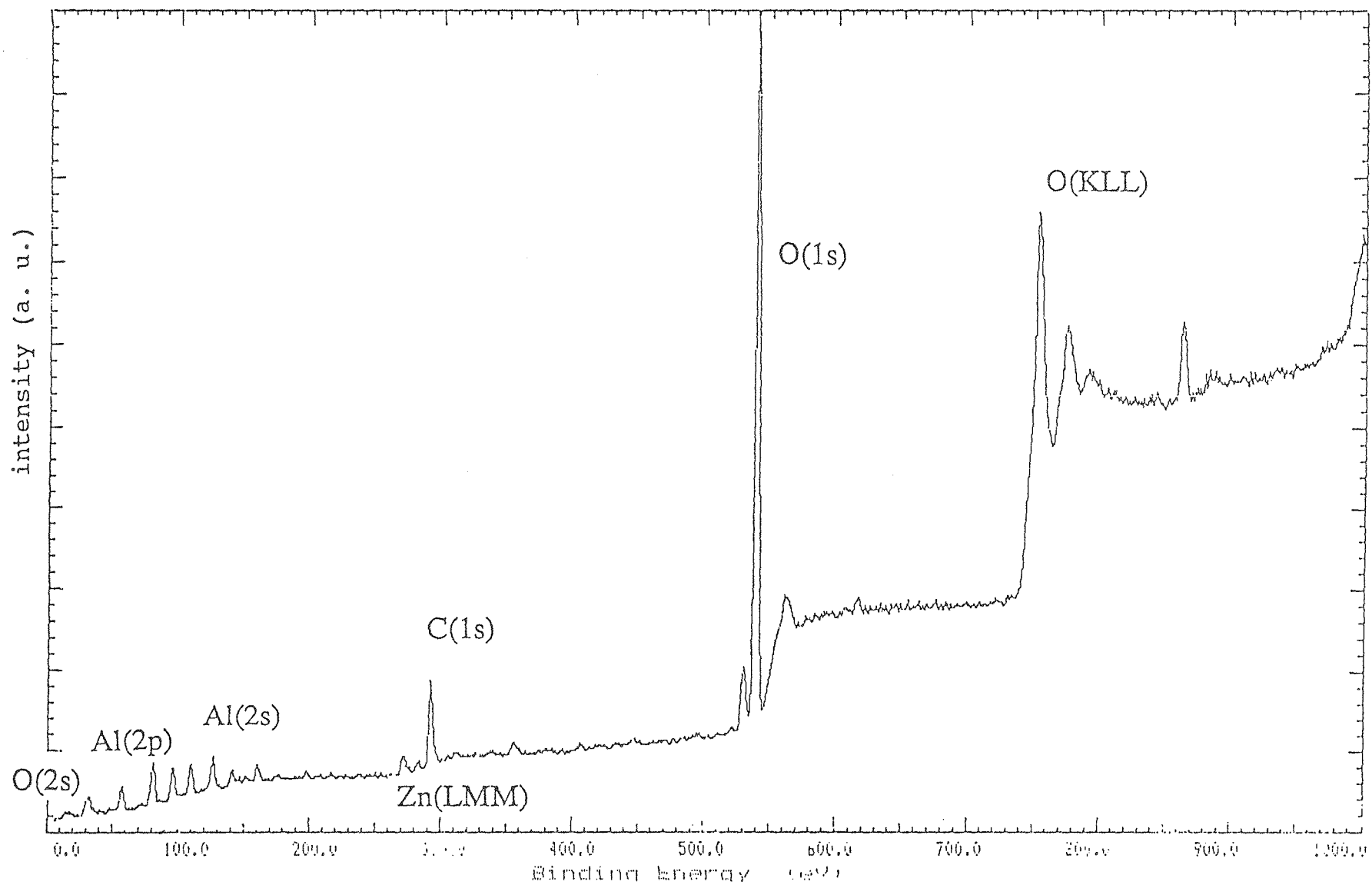
Fig. 8   The inside surface of a sample machined with Trimsol. The sample was not cleaned. Si and P peaks along with a rather intense Mg peak are present.
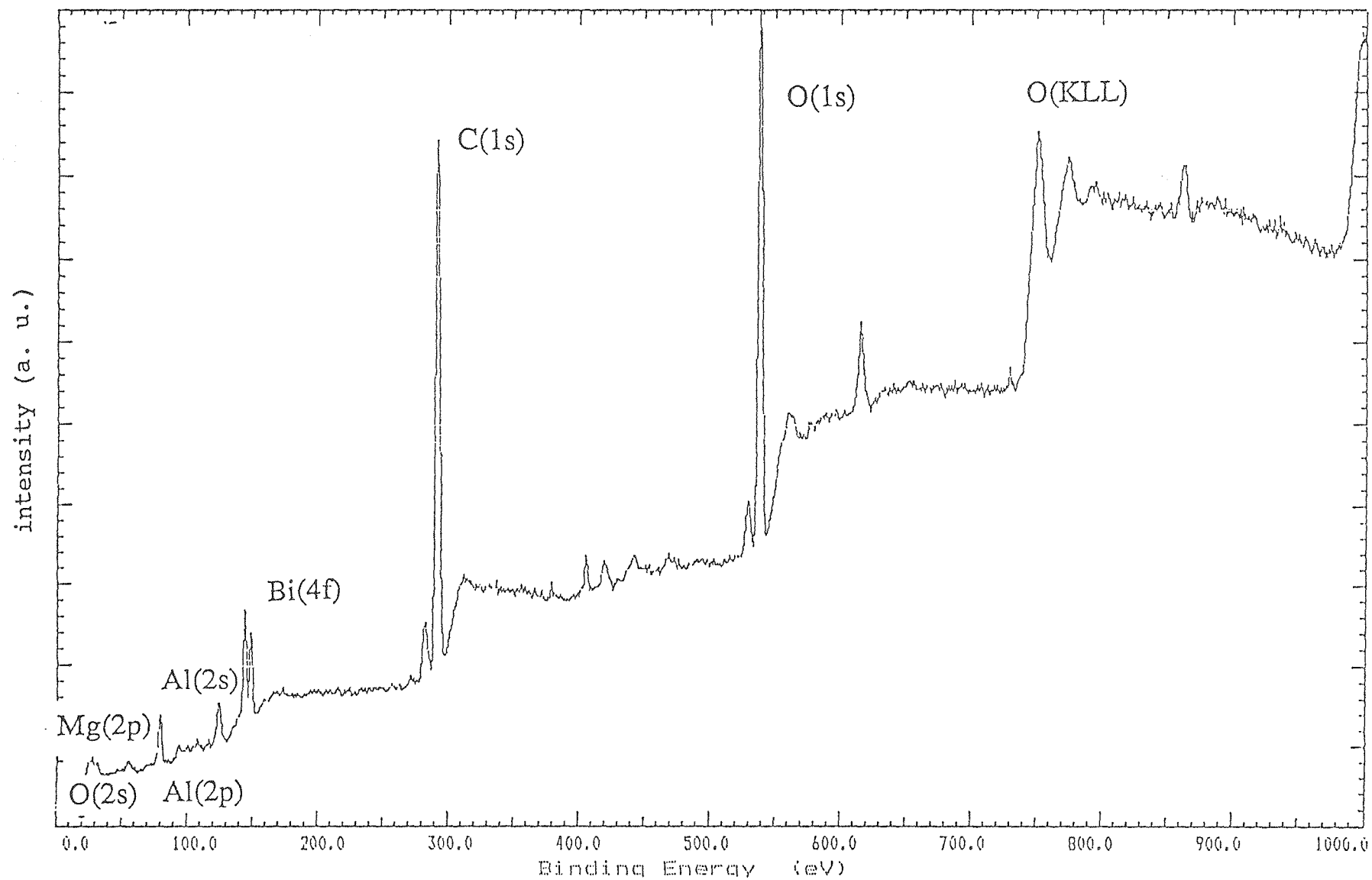
Fig. 9   The inside surface of a sample machined with Cimcool. Sample was not cleaned. There is significant contamination due to the coolant.
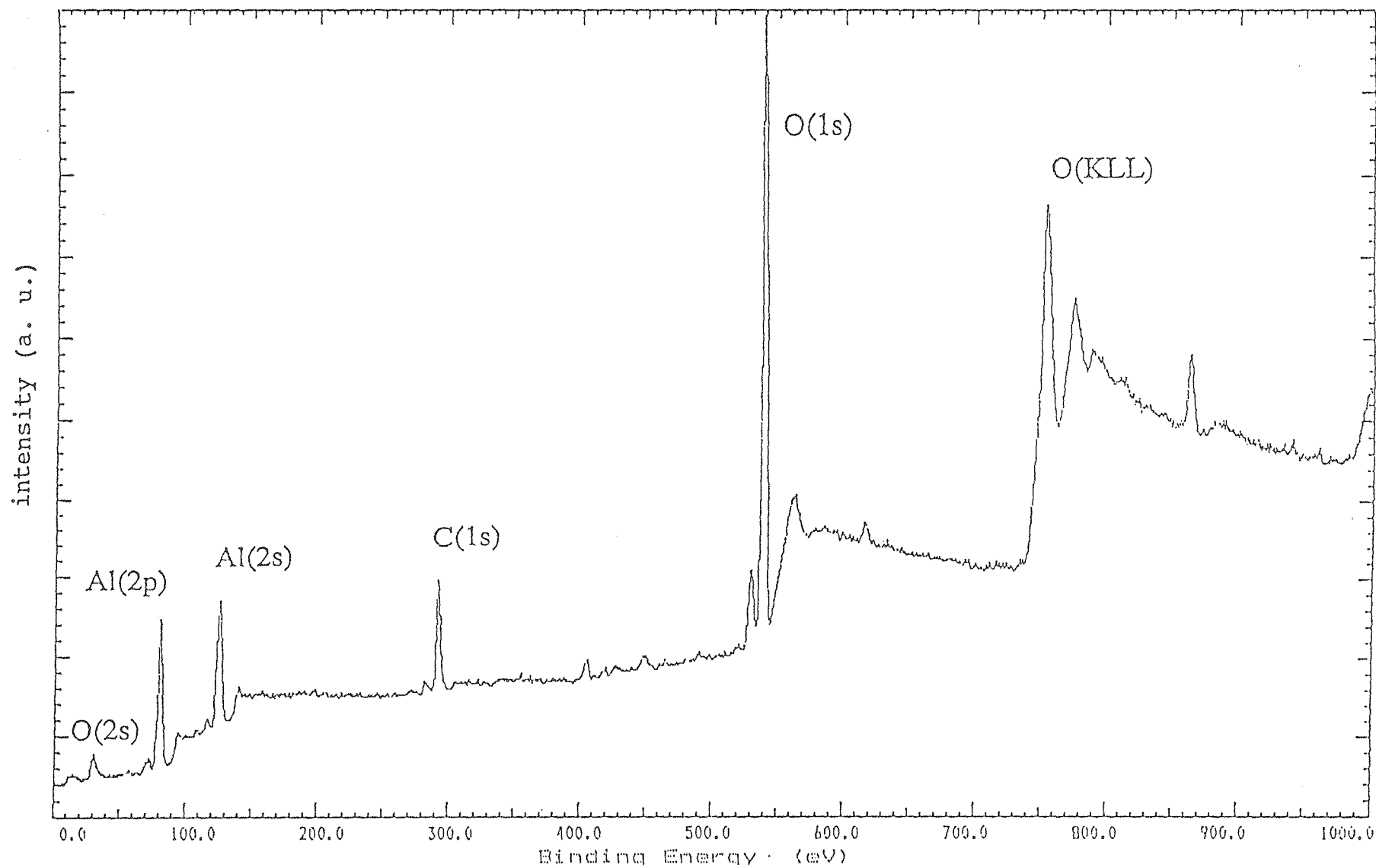
Fig. 10   The outside surface of a sample machined dry. Sample was cleaned. Cleaning has effectively removed the carbon residue. The two peaks at approximately 400 and 450 eV are Al ghosts. Cu(2p) peaks appear at 941 and 962 eV.
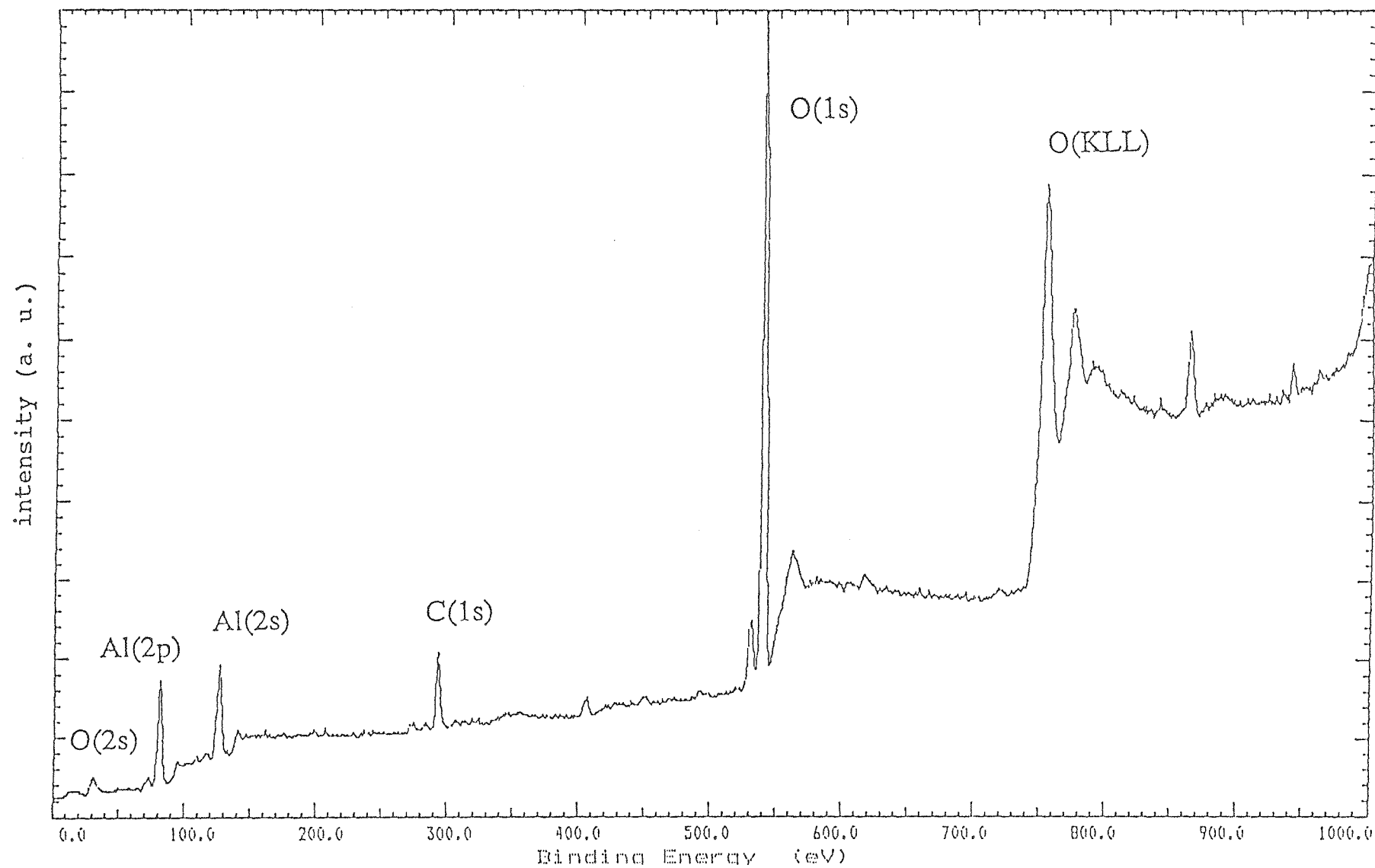
Fig. 11   The outside surface of a sample machined with Trimsol. Sample was cleaned. Cleaning has removed the coolant residue. Peaks are assigned as in Fig. 10.
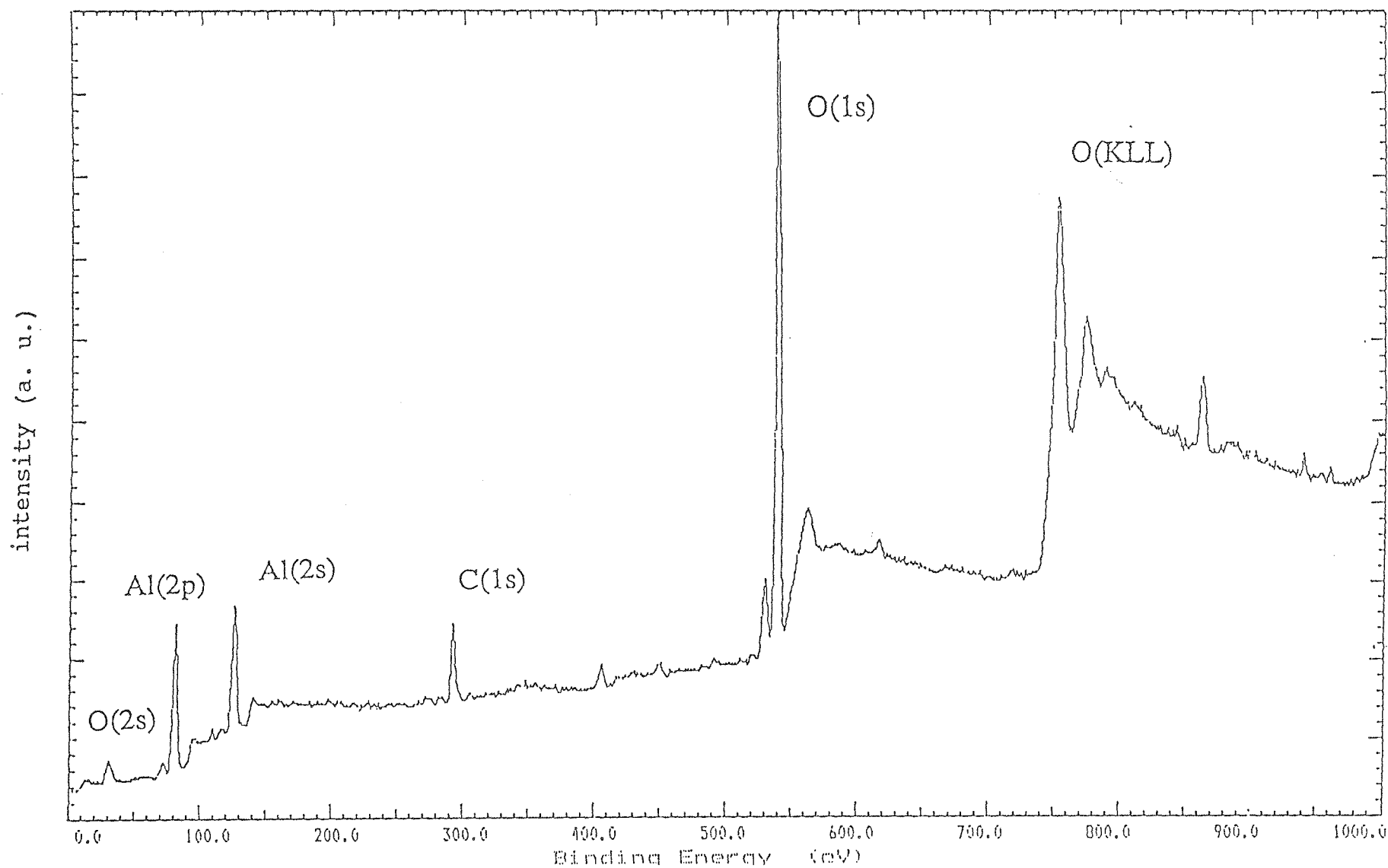
Fig. 12   The outside surface of a sample machined with Cimcool. Sample was cleaned leaving only carbon and oxygen as detectable adsorbates. Peaks are assigned as in Fig. 10.
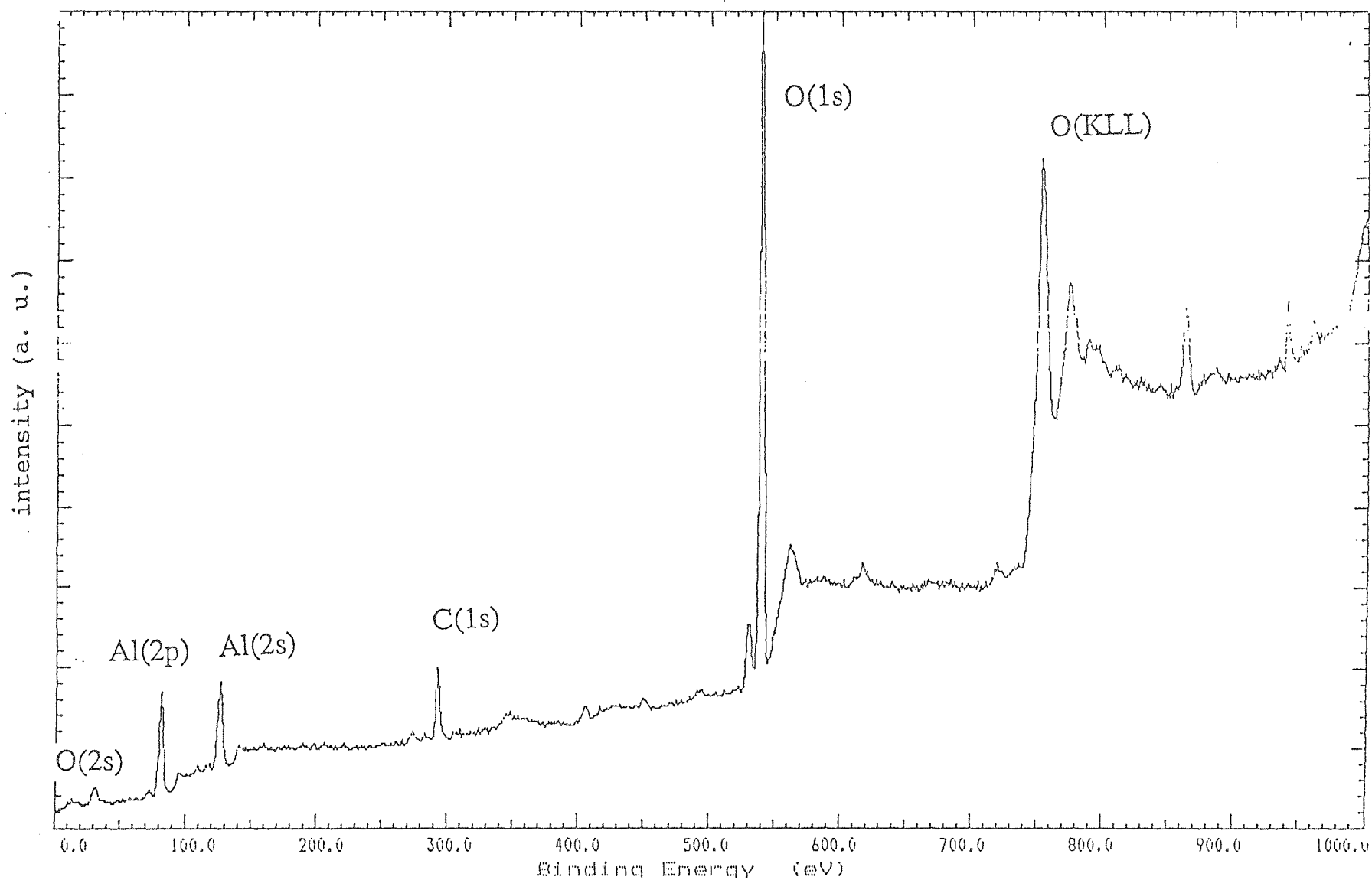
Fig. 13   The inside surface of a sample dry machined. Sample was cleaned. This spectrum is identical to spectra of samples which were machined with coolant and subsequently cleaned. Peaks are assigned as in Fig. 10.
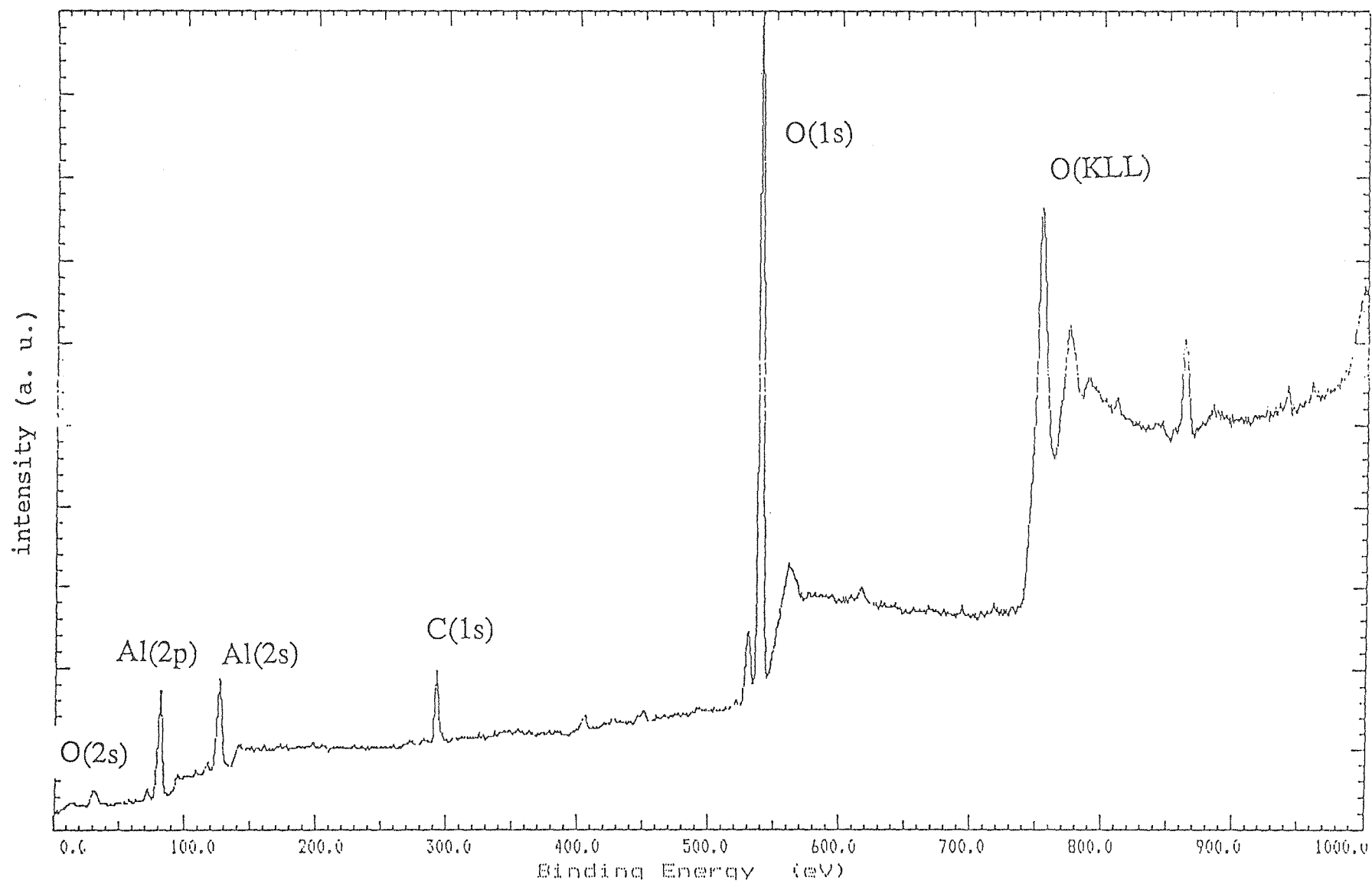
Fig. 14   The inside surface of a sample machined with Trimsol. Sample was cleaned. Peaks are assigned as in Fig. 10.
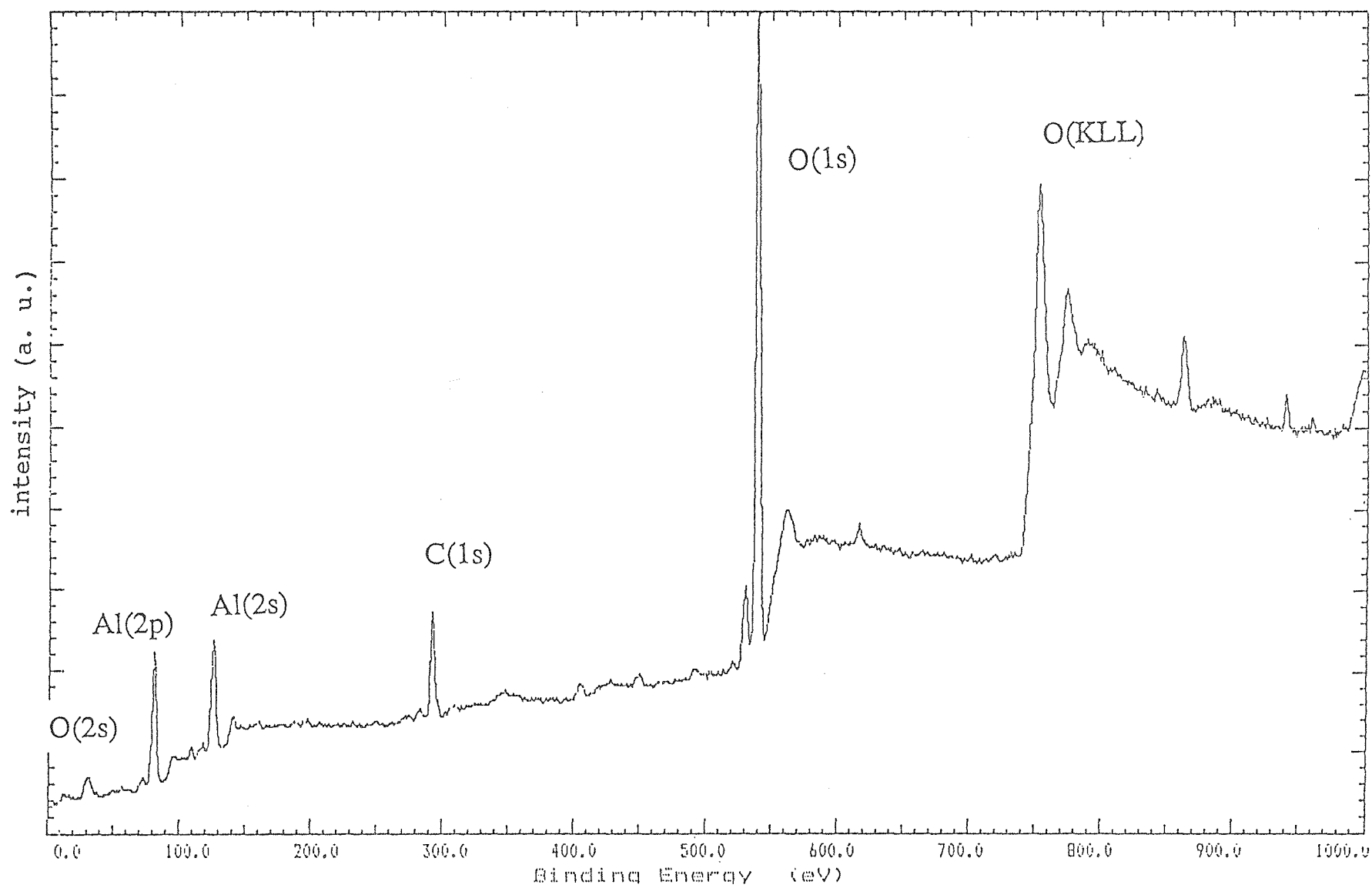
Fig. 15   The inside surface of a sample machined with Cimcool. Sample was cleaned. Peaks are assigned as in Fig. 10.
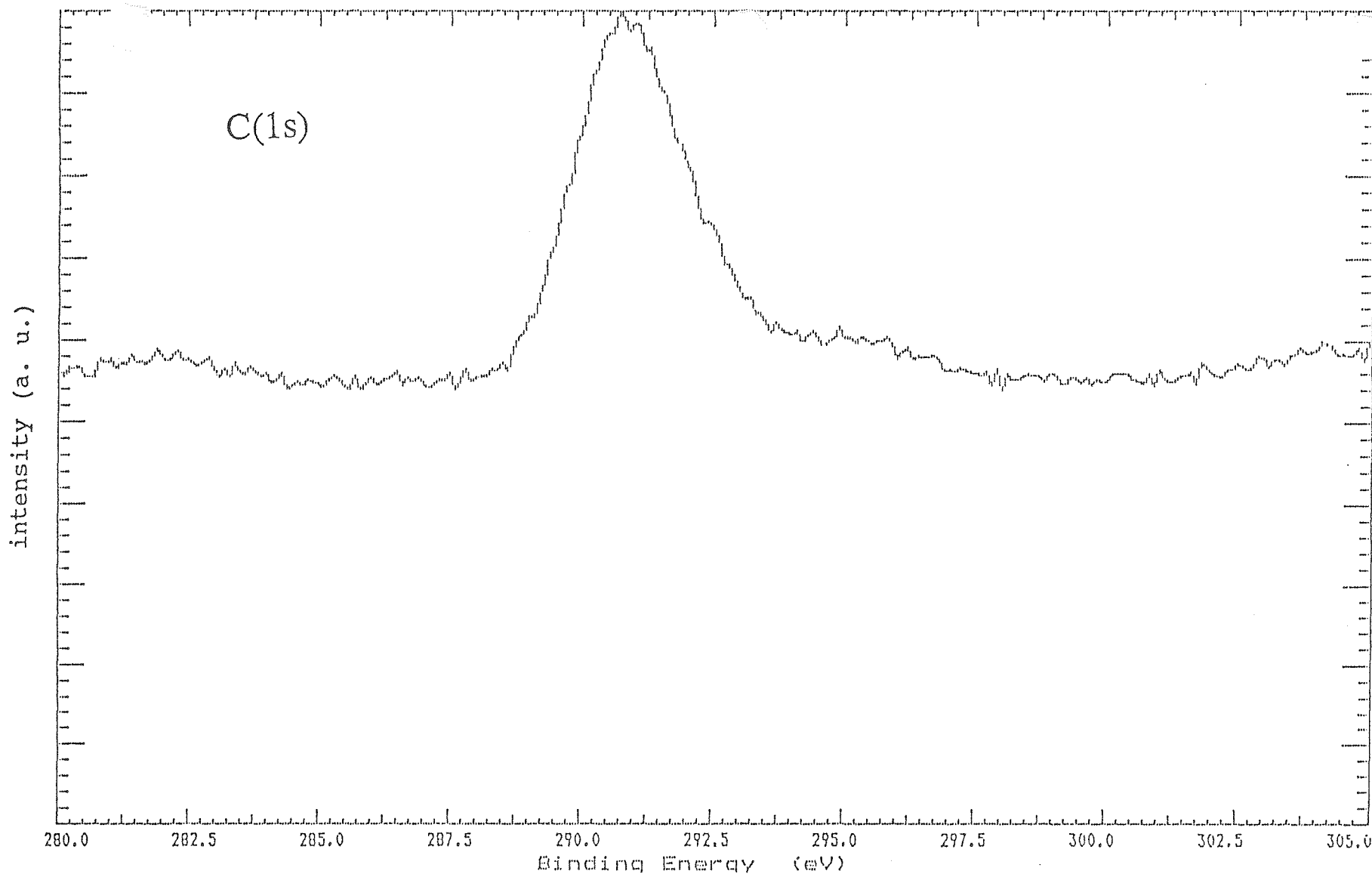
Fig. 16   The C(1s) region of Figure 13 indicating two forms of carbon on the surface. The larger intensity peak is due to carbon while the peak at higher binding energy results from an oxidized form of carbon. The binding energies are shifted to higher levels due to charging effects. However, the peak profiles are not typically affected by charging.